Acta Cryst. (1981). B**37**, 2228–2230

1,1,1,1,2,2,2,3,3,3-Decacarbonyl-2,3-μ-hydrido-2,3-μ-[hydrogen(phenyl)phosphido]-*triangulo*-triosmium

BY MARTIN J. MAYS, FRANTIŠEK PAVELČÍK,* PAUL R. RAITHBY, PHILIP L. TAYLOR AND PETER J. WHEATLEY

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

(*Received* 30 *March* 1981; *accepted* 26 *May* 1981)

Abstract. $C_{16}H_7O_{10}Os_3P$, $[Os_3H(CO)_{10}PH(C_6H_5)]$, monoclinic, $P2_1/n$ (limiting conditions, $h0l$: $h + l = 2n$; $0k0$: $k = 2n$), $a = 14{\cdot}273\ (4)$, $b = 8{\cdot}836\ (3)$, $c = 18{\cdot}033\ (5)$ Å, $\beta = 109{\cdot}16\ (2)°$, $U = 2148{\cdot}3$ Å^3, $Z = 4$, $D_c = 2{\cdot}967$ Mg m^{-3}, μ(Mo $K\alpha$) = 17·81 mm^{-1}; final $R = 0{\cdot}050$ for 2589 unique observed diffractometer data. The three Os atoms define an isosceles triangle with the longest edge bridged by both the hydride and the phosphide group. All the carbonyl ligands are terminal. The hydride ligand was not located directly but its position has been inferred from the distribution of the carbonyl ligands.

Introduction. Many Os complexes of general formula $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}X)]$ are known in which the X atom, which bridges the same edge of the Os_3 triangle as the H atom, formally acts as a three-electron donor. X-ray structural data are available for $[Os_3H(CO)_{10}SCH_2CH_3]$ (Allen, Mason & Hitchcock, 1977), $[Os_3H(CO)_{10}Cl]$ (Churchill & Lashewycz, 1979), and $[Os_3H(CO)_{10}NHSO_2C_6H_4Me]$ (Churchill, Hollander, Shapley & Keister, 1980), but complexes of this type containing a bridging phosphido ligand have not been studied previously. Indeed very few complexes containing this ligand are known.

The reaction of $Os_3(CO)_{12}$ with $PH_2(C_6H_5)$ in refluxing toluene (Iwasaki, Mays, Raithby, Taylor & Wheatley, 1981) gives, in addition to the mono- and disubstituted complexes $[Os_3(CO)_{11}\{PH_2(C_6H_5)\}]$ and $[Os_3(CO)_{10}\{PH_2(C_6H_5)\}_2]$, the complex $[Os_3H(CO)_{10}\{PH(C_6H_5)\}]$. For purposes of comparison with other complexes of this type an X-ray analysis of the latter complex has been undertaken.

Suitable crystals were obtained by slow evaporation of a hexane solution of the complex. 3726 reflections were measured for $3{\cdot}0 < 2\theta < 55{\cdot}0°$ on a Stoe four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation, an ω–θ scan technique and a crystal 0·29 × 0·26 × 0·10 mm. Lp corrections and a semi-empirical absorption correction based on a pseudo-ellipsoid model with 470 azimuthal scan data from 34 independent reflections were applied; transmission factors ranged from 0·248 to 0·938 for the full data set. The data were averaged to give 2589 unique observed reflections $[F > 4\sigma(F)]$. Cell dimensions were derived from the angular measurements of 20 strong reflections in the range $15 < 2\theta < 25°$.

The three Os atoms were located by multisolution Σ_2 sign expansion, and the C, N, O, and P atoms from a subsequent electron density difference synthesis. The structure was refined by full-matrix least squares with anisotropic thermal parameters assigned to all atoms. Complex neutral-atom scattering factors (*International*

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^3$)

$U_{eq} = \frac{1}{3}$ of the trace of the orthogonalized **U** matrix.

	x	y	z	U_{eq}
Os(1)	7572 (1)	3138 (1)	5301 (1)	36 (1)
Os(2)	6524 (1)	3158 (1)	3645 (1)	39 (1)
Os(3)	7990 (1)	5480 (1)	4313 (1)	32 (1)
P	7123 (3)	5732 (6)	5219 (2)	34 (3)
O(1)	8289 (15)	−85 (18)	5052 (13)	106 (23)
O(2)	5712 (10)	1947 (18)	5546 (10)	74 (14)
O(3)	8872 (10)	3104 (21)	7011 (8)	80 (18)
O(4)	9172 (10)	4672 (18)	3219 (9)	68 (13)
O(5)	6785 (13)	7886 (21)	3231 (9)	96 (16)
O(6)	9698 (9)	7532 (17)	5189 (9)	64 (12)
O(7)	4800 (9)	4923 (19)	3925 (10)	76 (15)
O(8)	8311 (12)	1421 (19)	3449 (10)	81 (15)
O(9)	5395 (12)	184 (17)	3644 (12)	84 (18)
O(10)	5730 (12)	3801 (21)	1881 (8)	85 (16)
C(1)	8020 (17)	1090 (28)	5134 (13)	68 (19)
C(2)	6405 (14)	2401 (23)	5470 (11)	46 (14)
C(3)	8367 (12)	3149 (22)	6381 (10)	44 (14)
C(4)	8728 (13)	4879 (19)	3632 (10)	39 (11)
C(5)	7266 (15)	7026 (23)	3620 (11)	53 (15)
C(6)	9043 (13)	6754 (22)	4870 (10)	43 (14)
C(7)	5458 (14)	4309 (22)	3856 (10)	45 (14)
C(8)	7657 (15)	2107 (20)	3518 (11)	47 (14)
C(9)	5825 (15)	1317 (22)	3608 (11)	52 (15)
C(10)	6042 (17)	3556 (26)	2535 (11)	64 (19)
C(11)	7531 (13)	7030 (19)	6054 (10)	36 (12)
C(12)	8513 (13)	6879 (24)	6581 (11)	51 (15)
C(13)	8776 (17)	8053 (28)	7199 (13)	64 (19)
C(14)	8142 (16)	9099 (26)	7257 (12)	57 (16)
C(15)	7177 (16)	9190 (24)	6741 (11)	54 (16)
C(16)	6874 (13)	8132 (21)	6103 (10)	38 (11)

---

* Permanent address: Department of Analytical Chemistry, Faculty of Pharmacy, Comenius University, 88034 Bratislava, Czechoslovakia.

0567-7408/81/122228-03$01.00

Table 2. *Bond lengths* (Å)

Os(1)—Os(2)	2·868 (4)	Os(1)—Os(3)	2·917 (4)
Os(1)—P	2·372 (7)	Os(1)—C(1)	1·98 (3)
Os(1)—C(2)	1·90 (2)	Os(1)—C(3)	1·91 (2)
Os(2)—Os(3)	2·896 (4)	Os(2)—C(7)	1·97 (2)
Os(2)—C(8)	1·94 (2)	Os(2)—C(9)	1·90 (2)
Os(2)—C(10)	1·92 (2)	Os(3)—P	2·361 (7)
Os(3)—C(4)	1·94 (2)	Os(3)—C(5)	1·91 (2)
Os(3)—C(6)	1·88 (2)	P—C(11)	1·83 (2)
O(1)—C(1)	1·13 (3)	O(2)—C(2)	1·12 (3)
O(3)—C(3)	1·13 (2)	O(4)—C(4)	1·14 (3)
O(5)—C(5)	1·11 (3)	O(6)—C(6)	1·15 (2)
O(7)—C(7)	1·13 (3)	O(8)—C(8)	1·15 (3)
O(9)—C(9)	1·19 (3)	O(10)—C(10)	1·14 (3)
C(11)—C(12)	1·42 (2)	C(11)—C(16)	1·37 (3)
C(12)—C(13)	1·48 (3)	C(13)—C(14)	1·32 (4)
C(14)—C(15)	1·39 (3)	C(15)—C(16)	1·44 (3)

Table 3. *Bond angles* (°)

Os(2)—Os(1)—Os(3)	60·1 (1)	Os(2)—Os(1)—P	83·8 (2)
Os(3)—Os(1)—P	51·8 (2)	Os(2)—Os(1)—C(1)	86·1 (7)
Os(3)—Os(1)—C(1)	114·6 (9)	P—Os(1)—C(1)	166·0 (7)
Os(2)—Os(1)—C(2)	89·1 (6)	Os(3)—Os(1)—C(2)	134·9 (5)
P—Os(1)—C(2)	96·2 (7)	C(1)—Os(1)—C(2)	93·2 (11)
Os(2)—Os(1)—C(3)	175·2 (6)	Os(3)—Os(1)—C(3)	116·6 (7)
P—Os(1)—C(3)	96·7 (7)	C(1)—Os(1)—C(3)	92·6 (9)
C(2)—Os(1)—C(3)	95·6 (9)	Os(1)—Os(2)—Os(3)	60·8 (1)
Os(1)—Os(2)—C(7)	88·5 (6)	Os(3)—Os(2)—C(7)	93·0 (6)
Os(1)—Os(2)—C(8)	87·1 (6)	Os(3)—Os(2)—C(8)	82·6 (6)
C(7)—Os(2)—C(8)	174·9 (7)	Os(1)—Os(2)—C(9)	96·9 (7)
Os(3)—Os(2)—C(9)	157·1 (5)	C(7)—Os(2)—C(9)	91·0 (10)
C(8)—Os(2)—C(9)	92·0 (10)	Os(1)—Os(2)—C(10)	166·2 (7)
Os(3)—Os(2)—C(10)	105·5 (8)	C(7)—Os(2)—C(10)	94·1 (10)
C(8)—Os(2)—C(10)	89·6 (10)	C(9)—Os(2)—C(10)	96·7 (10)
Os(1)—Os(3)—Os(2)	59·1 (1)	Os(1)—Os(3)—P	52·1 (2)
Os(2)—Os(3)—P	83·3 (2)	Os(1)—Os(3)—C(4)	117·1 (6)
Os(2)—Os(3)—C(4)	90·6 (6)	P—O(3)—C(4)	169·2 (5)
Os(1)—Os(3)—C(5)	137·0 (7)	Os(2)—Os(3)—C(5)	94·2 (7)
P—Os(3)—C(5)	95·2 (8)	C(4)—Os(3)—C(5)	94·1 (9)
Os(1)—Os(3)—C(6)	112·7 (7)	Os(2)—Os(3)—C(6)	170·8 (5)
P—Os(3)—C(6)	94·8 (7)	C(4)—Os(3)—C(6)	89·8 (9)
C(5)—Os(3)—C(6)	95·0 (9)	Os(1)—P—Os(3)	76·1 (3)
Os(1)—P—C(11)	123·2 (6)	Os(3)—P—C(11)	122·1 (8)
Os(1)—C(1)—O(1)	178·8 (21)	Os(1)—C(2)—O(2)	177·7 (16)
Os(1)—C(3)—O(3)	176·3 (17)	Os(3)—C(4)—O(4)	173·3 (16)
Os(3)—C(5)—O(5)	174·7 (22)	Os(3)—C(6)—O(6)	177·8 (18)
Os(2)—C(7)—O(7)	174·7 (14)	Os(2)—C(8)—O(8)	176·9 (18)
Os(2)—C(9)—O(9)	175·0 (19)	Os(2)—C(10)—O(10)	178·0 (22)
P—C(11)—C(12)	118·1 (15)	P—C(11)—C(16)	117·2 (12)
C(12)—C(11)—C(16)	124·7 (17)	C(11)—C(12)—C(13)	112·9 (19)
C(12)—C(13)—C(14)	122·7 (19)	C(13)—C(14)—C(15)	122·8 (21)
C(14)—C(15)—C(16)	118·1 (21)	C(11)—C(16)—C(15)	118·7 (16)

Tables for X-ray Crystallography, 1974) were employed, and in the final cycles of refinement a weighting scheme of the form $w = [\sigma^2(F) + 0{\cdot}0008|F|^2]^{-1}$ was introduced. The final residuals were $R = 0{\cdot}050$ and $R_w = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o| = 0{\cdot}048$. A final difference map revealed no significant regions of electron density and the H atoms were not located. Final atomic coordinates and equivalent isotropic temperature factors are given in Table 1, and bond lengths and angles in Tables 2 and 3.*

Discussion. The analysis shows that the crystal structure consists of discrete $[Os_3H(CO)_{10}PH(C_6H_5)]$ molecules separated by normal van der Waals distances. The molecular structure (Fig. 1) is closely related to that of $[Ru_3H(CO)_{10}PH(C_6H_5)]$ (Iwasaki, Mays, Raithby, Taylor & Wheatley, 1981), but the crystal structures are not isomorphous. The three Os atoms define a slightly distorted isosceles triangle. The Os(1)—Os(3) edge is bridged by both the $PH(C_6H_5)$ group and the hydride ligand. The hydride was not located directly but its presence was inferred from the bending away of the carbonyl groups adjacent to the bridged edge and by analogy with other structures. The Os(1)—Os(3) distance is significantly longer than the other two Os—Os distances but not to such an extent as in the analogous Ru complex. The carbonyl groups are all terminal and approximately linear with an average Os—C—O angle of 176 (3)°.

The Os(2) atom has a distorted octahedral coordination geometry with the equatorial Os—C distances [mean 1·91 (3) Å] shorter than the axial distances [mean 1·96 (3) Å]. This is in keeping with the greater competition between *trans* carbonyls for back donation from the same metal orbital, and results in the lengthening of the two axial Os—C bonds.

The P atom of the $PH(C_6H_5)$ ligand symmetrically bridges the Os(1)—Os(3) edge, and the dihedral angle between the Os_3 and Os_2P planes is 107·1 (2)°. The phenyl ring is planar and the $P(C_6H_5)$ plane is approximately perpendicular to the Os_3 and Os_2P planes with dihedral angles of 99·5 (2) and 85·6 (2)° respectively. The phenyl ring is orientated away from the metal triangle while the less bulky H atom bonded to P lies closer to the Os(1)—Os(3) edge.

We thank the Science Research Council for financial support, Johnson Matthey & Co. Ltd for a grant (to PLT), and the British Council for a grant (to FP). Calculations were performed on the University of Cambridge IBM 370/165 computer with *SHELX* 76 (Sheldrick, 1976); the figure was drawn with *ORTEP* (Johnson, 1965).

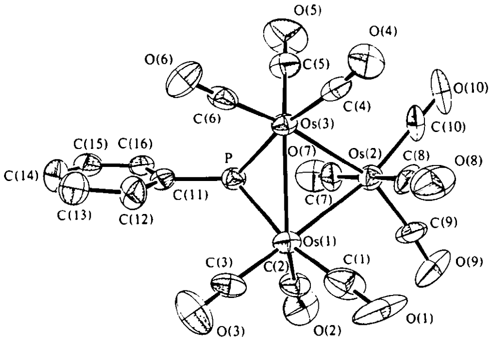


Fig. 1. The molecular structure of $[Os_3H(CO)_{10}PH(C_6H_5)]$.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36197 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

ALLEN, V. F., MASON, R. & HITCHCOCK, P. B. (1977). *J. Organomet. Chem.* **140**, 297–307.

CHURCHILL, M. R., HOLLANDER, F. J., SHAPLEY, J. R. & KEISTER, J. B. (1980). *Inorg. Chem.* **19**, 1272–1277.

CHURCHILL, M. R. & LASHEWYCZ, R. A. (1979). *Inorg. Chem.* **18**, 1926–1930.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

IWASAKI, F., MAYS, M. J., RAITHBY, P. R., TAYLOR, P. L. & WHEATLEY, P. J. (1981). *J. Organomet. Chem.* **213**, 185–206.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

SHELDRICK, G. M. (1976). *SHELX* 76. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1981). B**37**, 2230–2232

1,1,1,1,2,2,2,3,3,3-Decacarbonyl-2,3-μ-hydrido-2,3-μ-trifluoroethylideneamido-*triangulo*-triosmium

BY MICHAEL LAING AND POLLY SOMMERVILLE

Chemistry Department, University of Natal, Durban 4001, *South Africa*

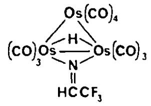
AND PETER J. WHEATLEY, MARTIN J. MAYS AND ZAIN DAWOODI

*University Chemical Laboratory, Lensfield Road, Cambridge CB*2 1*EW, England*

(*Received* 11 *March* 1981; *accepted* 1 *June* 1981)

Abstract. $[Os_3H(CO)_{10}N(CHCF_3)]$, M_r = 947·6, monoclinic, $P2_1/n$, a = 7·321 (5), b = 29·21 (1), c = 9·364 (5) Å, β = 100·55 (5)°, V = 1968·9 Å^3, D_c = 3·196, D_m = 3·20 (5) Mg m^{-3}, Z = 4, μ(Mo $K\alpha$) = 20·63 mm^{-1}. R = 0·103 for 2763 observed data. The Os atoms form a triangle of one $Os(CO)_4$ group and two $Os(CO)_3$ groups. The N of the CF_3CN molecule bridges the two $Os(CO)_3$ groups. One H is attached to the C of the nitrile group, the second is presumed to remain as an Os—H—Os bridge.

Introduction. Reaction of $[H_2Os_3(CO)_{10}]$ with the nitrile CF_3CN yields two isomeric compounds of stoichiometry $[H_2Os_3(CO)_{10}(CF_3CN)]$. The ^1H NMR spectrum of the major product (I) contains only one metal hydride resonance and a one-proton quartet assignable to a $CHCF_3$ proton, suggesting that a hydride transfer has taken place. To ascertain the precise mode of bonding of the CF_3—CHN group to the Os_3 triangle, a crystallographic study of (I) was undertaken.



(I)

Suitable crystals were obtained by cooling a saturated hexane solution to 268 K. Data were collected from a crystal 0·3 × 0·3 × 0·3 mm on a Philips four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·7107 Å) for $3° < \theta < 25°$ and index $k \leq 30$. The small separation between reflexions caused by the long b axis prevented individual backgrounds being measured for each reflexion, so the background correction was based entirely on the value of the angle θ. Of 3461 reflexions measured, 2763 were classed as observed $[I > 2{\cdot}0\sigma(I)]$.

The intensities of the three standard reflexions dropped by about 7% during the course of data collection. Because of this decomposition and the imprecision of the background correction, only Lorentz and polarization corrections were applied to the intensities. A temperature-sharpened Patterson map (Lipson & Cochran, 1966) gave the coordinates of the three Os atoms, and subsequent Fourier maps yielded the coordinates of the lighter atoms. The structure was refined by block-diagonal least squares with the three Os atoms assigned anisotropic temperature factors. Weighting was proportional to $1/\sigma(F)$. Scattering factors were for neutral atoms (*International Tables for X-ray Crystallography*, 1962); that of Os was corrected for anomalous dispersion. The H atoms could not be located. The final R was 0·103 for 2763 observed data.* The relatively high value of R is to

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36201 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0567-7408/81/122230-03\$01.00